

Direct Determination of Total Organic
Chlorine in Water without Preconcentration

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DIRECT DETERMINATION OF TOTAL ORGANIC CHLORINE
IN WATER WITHOUT PRECONCENTRATION

by

Judith A. Gebhardt
Gulf South Research Institute
New Orleans, Louisiana 70186

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Project Officer

Stephen Billets
Environmental Monitoring and Support Laboratory
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati, conducts research to:

- Develop and evaluate methods to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria, and other microbiological organisms in water; and, to determine the responses of aquatic organisms to water quality.
- Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.
- Develop and operate a computerized system for instrument automation leading to improved data collection, analysis, and quality control.

In accordance with these objectives, Gulf South Research Institute conducted the project reported here to develop instrumentation for the direct determination of total chlorinated organic compounds in aqueous samples without preconcentration.

Robert L. Booth

Robert L. Booth, Acting Director
Environmental Monitoring and Support
Laboratory - Cincinnati

ABSTRACT

The goal of this research effort was to develop instrumentation for the direct determination of total chlorinated organic compounds in aqueous samples without preconcentration. Two general approaches were investigated. The first involved isolation of the chlorinated organics from the sample matrix by flash evaporation. A catalytic conversion step was to produce free chlorine which was to be detected and quantified fluorometrically. This approach did not prove successful. An alternate procedure was investigated which used a piezoelectric crystal as the detection device. After evaluating a number of crystal coatings, Amine 220 was found to have appropriate characteristics. This material, a gas chromatographic stationary phase, has a high affinity for hydrochloric acid (HCl) and almost none for sodium chloride (NaCl) which is a major interference in total organic chloride (TOCl) or total organic halogen (TOX) determinations. In this procedure, the sample was delivered to the detector system by a direct injection of the aqueous sample through a quartz tube which is heated to approximately 600°C. Use of oxygen as the carrier gas created the oxidizing environment in which the chlorinated organics are converted to HCl.

The piezoelectric crystal coated with Amine 220 was found to have an absolute detection limit of approximately 100 pg of HCl. Assuming a minimum of 50 percent conversion efficiency, approximately three parts per billion (weight/volume) of chloroform should be detectable in a 100 μ L aqueous sample. Difficulties were encountered in removing water from the system before it reached the detector system. Large amounts of water in contact with the Amine 220 coated piezoelectric crystal saturated the detector. Several modifications in the sample delivery system were investigated to remove the water. None were entirely successful, and additional work is necessary before the system is ready for further field evaluations.

This report was submitted in fulfillment of Grant No. R-805340010 by Gulf South Research Institute under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period June 26, 1978 to June 25, 1981, and work was completed as of April 20, 1982.

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SECTION 1

INTRODUCTION

There is continuing interest in the determination of halogenated organics in aqueous samples. This interest stems from the suspected health risks posed by these compounds and from the realization that the chlorination disinfection process used by many municipal treatment facilities results in the generation of this class of compounds (1,2).

Many analytical procedures focus on the identification and quantification of specific halogenated compounds (3). These methods tend to be labor intensive and time consuming and have been found, in some instances, to account for only 25 percent of the halogenated organic compounds in aqueous samples (4). Because of the importance of the determination of halogenated organics as a general indication of water quality, research efforts have emphasized the development of rapid reliable methods for the determination of total organic halides in aqueous samples.

Among the early work in this area is that reported by Kuhn and Sontheimer (5,6). This procedure involves stirring a 10 L sample with 1 g of activated carbon. After stirring for one hour, the carbon is settled by flocculation and the bulk of the sample siphoned off. Fresh carbon is added to the sample and stirring is repeated. When the adsorption step is completed, the two 1-g portions of carbon are recovered by filtration and the recovered sludge cakes are pyrohydrolyzed to convert adsorbed chlorinated organics to HCl which is recovered by condensation. Chloride ion content in the resulting sample is determined using an ion-selective electrode. Correction for the positive interference caused by the presence of inorganic chloride in the sample is made by preparing a duplicate sample as described above and stirring the recovered sludge cakes with sodium nitrate prior to pyrohydrolysis.

Similar procedures involve the use of small packed columns of activated carbon (7,8) to achieve analyte concentration, adding nitrate to the original sample to hinder inorganic chloride adsorption (8), controlled combustion to generate HCl (6), and the use of microcoulometry to quantify the converted halogens (7,9-10).

Alternate procedures for TOX determination using XAD resins as the adsorption medium have been suggested (11). However, these studies and work

conducted in our laboratories demonstrate that the macroreticular resins investigated do not have good affinity for the entire spectrum of organic halide volatility types. The data generated by the use of these procedures generally provides a low estimate of the levels of chlorinated organics in aqueous samples.

A carbon adsorption method has been automated by the Dohrmann Company (DX-20). This system incorporates an adsorption module (AD-2) containing 40 ± 5 mg of activated carbon in a Pyrex mini-column, a two stage pyrolysis unit, and an on-line microcoulometric detection cell. The water sample is acidified to pH 2 with concentrated nitric acid (HNO_3) to improve the adsorption of organics and pumped through two mini-columns placed in series. The mini-columns are then flushed with a nitrate solution to displace inorganic chloride ions. The contents of each mini-column is transferred individually to a quartz boat. Pyrolysis takes place in two stages. The first stage involves heating at 200°C for two minutes in a carbon dioxide rich atmosphere. The quartz boat is then advanced to an 800°C oxygen rich atmosphere for six to ten minutes. The effluent gases are titrated directly in the microcoulometric detection cell. In general, the recovery for most halogenated organics is 90 percent or better and the limit of sensitivity is $5 \mu\text{g/L}$ (9).

The research presented in this report was designed to investigate a different approach. The objective of these investigations was to develop a system for the direct determination of the total organic chlorine content of aqueous samples without preconcentration of the sample. The result of these efforts has been to identify an approach which promises several advantages over previously reported methods. This system involves a heated injection unit for direct introduction of the aqueous sample into a heated quartz tube in which the chlorinated organics are converted to hydrochloric acid. This compound is then swept into a detector cell which contains a piezoelectric crystal coated with Amine 220. This detector is very sensitive and highly selective for the hydrochloric acid. Application to brominated and iodinated organic compounds must still be investigated.

This technique eliminates the need for sample preconcentration and, consequently, one of the major sources of imprecision in TOX methodologies. It shows promise as a rapid, reliable procedure which lends itself to on-line monitoring of drinking water supplies. The research reported here was conducted under funding provided by EPA Grant No. R805340010. Work on the promising piezoelectric crystal system was conducted over a six month period of time and represents approximately one man year of effort.

SECTION 2

SUMMARY

This report describes research undertaken to develop a method for direct determination of total halogenated organic compounds in aqueous samples without preconcentration. The approach, which promises to be successful, consists of an injection system for the introduction of the aqueous sample, a heated quartz tube for the conversion of chlorinated organics to HCl, a device for removal of water from the carrier gas stream, and a piezoelectric crystal coated with Amine 220 which is a very sensitive and highly selective detector for hydrochloric acid.

The system developed as a result of this research was demonstrated to have a detection limit of approximately 100 pg HCl. This means that approximately three parts per billion (weight/volume) of chloroform could be detected in an aqueous sample assuming at least 50 percent efficiency of the conversion to HCl. This analysis can be performed using 100 μ L of sample, injected directly into the analyzer.

The procedure requires further work before the system is ready for field evaluation. The presence of water vapor in the carrier gas stream as it reaches the piezoelectric crystal saturates the detector and eliminates low level response. Therefore it is necessary to remove the water in order to detect trace amounts of HCl. Several procedures to remove the H₂O interference were investigated and one was developed which was partially successful. However, this procedure also affected the sensitivity of the system. Further experimentation is necessary to solve this problem.

SECTION 3

CONCLUSIONS AND RECOMMENDATIONS

This research effort has resulted in the identification of a promising technique for the determination of the total organic chlorine content in aqueous samples. The procedure is sensitive and highly selective for chlorinated organic compounds, it requires a very small sample volume and no sample preconcentration. The procedure takes approximately five minutes from the time the sample is presented to the system until the raw data is received.

Two components of the system require further work before the procedure is ready for further field evaluation. First is optimization of the conversion of chlorinated organics to HCl. Under the oven temperature and carrier gas flow rate conditions used in this work, the conversion efficiency was estimated to be approximately 10 percent. Increasing the efficiency of this step will improve the sensitivity of the technique. The second component of the system which requires improvement is that which removes water from the carrier gas stream before it reaches the detector. The piezoelectric detector responds proportionally to the total amount of material deposited on it. Coating the crystal with Amine 220 renders it insensitive to small amounts of materials other than HCl which is produced from the halogenated organics in the sample. However, the relatively large amounts of water condensed on the crystal producing a large false positive signal. Various attempts to remove the water before it reached the piezoelectric crystal were not entirely successful. Further experimentation is required to perfect this aspect of the system.

This research effort has demonstrated the feasibility of a system for the direct determination of halogenated organics in water. Perhaps more importantly, however, the potential of a new detector system, the piezoelectric crystal, has been realized. For this work the crystal was coated with Amine 220 to make it specific for HCl, HBr, and HI. It is also possible to coat crystals with materials which will make the detector selectively responsive to other groups of compounds such as organophosphates or nitrogen containing compounds. The crystals themselves are inexpensive and commercially available. The possibilities for using a coated piezoelectric crystal to analyze water for a variety of specific chemical classes should be investigated. Such instrumentation, providing sensitive, easy, reliable screening data, would be of immense benefit in monitoring effluents from municipal or industrial treatment processes or even in field situations when the general nature of a spill must be identified.

SECTION 4

TECHNICAL APPROACH

SYSTEM I

The first system which was investigated for the determination of halogenated organics in water involved: (a) flash evaporation to separate chlorinated organics from inorganic chloride salts; (b) oxidation of organic chlorides to free chlorine in a catalytic combustion furnace; (c) derivatization of the free chlorine with syringaldazine; and (d) fluorometric determination of the resulting fluorescent derivative.

Flash Evaporator

Model I--

Design of the first flash evaporation apparatus investigated is shown in Figure 1. This evaporator consisted of a Pyrex tube one inch in diameter by nine inches long, similar to a Vigreux distillation column, mounted in a horizontal position. Indentations in the tube provided a large surface area and heat sink for sample flash evaporation. The evaporation tube could be heated to 400°C when wrapped with heating tape. Higher temperatures were attainable when the heating tape was replaced with coiled Chromel resistance heating wire. Thermocouple sensors were used to monitor cylinder and surface temperatures of the flash evaporator.

Condenser traps were cold fingers cooled with liquid nitrogen. The trap nearest the evaporator was used to promote rapid, reliable condensation. The other was for backup purposes and, with the activated carbon trap, prevented vacuum pump vapors from backstreaming into the system.

Evaporation at atmospheric pressure was conducted in a closed system; vacuum micro and macro needle valves were closed to isolate the pump. Controlled evaporation under vacuum was possible by opening the needle valves and monitoring the system vacuum with thermocouple gauges connected to the vacuum stopcocks. The pump was rated at 150 L/min.

Buffered water samples, pH 9.0 with 1 mM sodium borate, were contained in a 10-mL glass syringe connected to a stainless steel delivery tube. Sample injection rate varied from 0.2 to 2 mL/min and was controlled by the three-way stopcock. Forces exerted on the delivery tube by the syringe barrel and the hydrostatic head were sufficient for gravity feed of the sample to the evaporator during atmospheric pressure experiments.

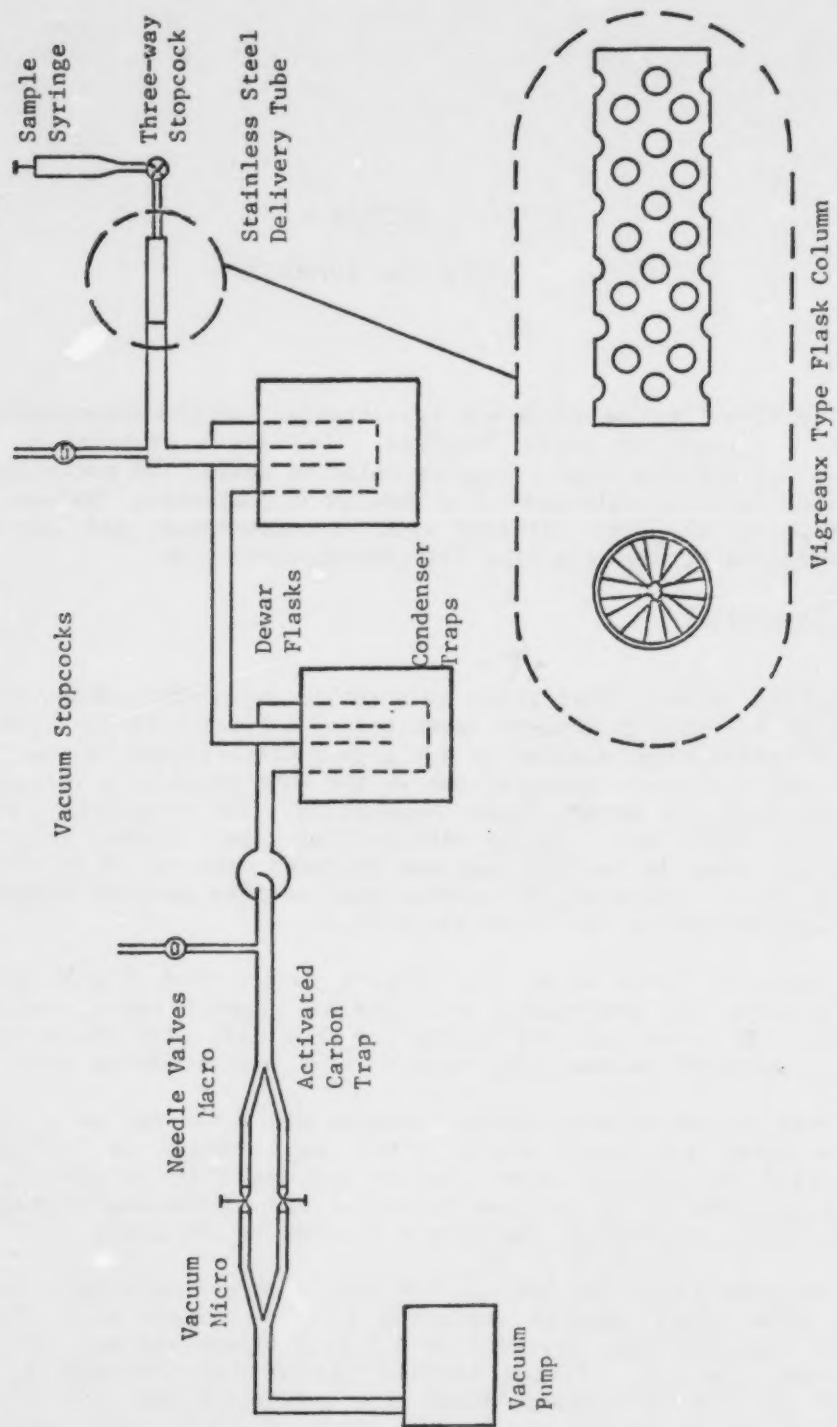


Figure 1. Model I: horizontal flash evaporation apparatus.

Generally, evaluation of the horizontal evaporator was carried out at 400°C and 100-500 millitorr. Flash evaporation of 250 ppm NaCl in sodium borate buffer at pH 9.0 resulted in a high carry-over of chloride, approximately 40-50 percent. Chloride was determined by standard chloride titration with $\text{Hg}(\text{NO}_3)_2$. The flash evaporator column was then packed with 3 mm glass beads in an attempt to reduce NaCl carry-over. However, approximately 40 percent of the chloride was still carried over. Chloride carry-over was also unacceptable at atmospheric pressure evaporation.

Model II--

This design (Figure 2) is similar to the first design except for the following changes. The horizontal flash evaporator was replaced with a Pyrex gravity separator, 3 x 9 inches. This flask was placed in a muffle furnace positioned on its back with the door removed. The muffle furnace provided a convenient heat source for various flash evaporator geometries.

A 1 cm layer of 3-5 mm glass beads was placed in the bottom of the evaporator flask to increase surface area heated. The transfer line connected to the evaporator and liquid nitrogen trap was wrapped with heating tape to prevent condensation on cold spots. Two sample syringes were used. The one positioned nearest the micro needle control valve was filled with charcoal treated water; the other contained buffered sample. A needle control valve was used to control sample evaporation rate. Syringe stopcocks functioned as on-off valves. After sample injection, the delivery tube was flushed with a small volume of treated water.

This model was developed to overcome problems encountered with the first flash evaporator. Loosely packed glass wool was placed in the transfer line between the evaporator and cold trap to enhance vapor-particulate separation. Experiments with this second apparatus were conducted at 400°C and ambient and subambient pressures using Na^{36}Cl , $^{14}\text{CHCl}_3$, and a mixture of ^{14}C -polychlorinated biphenyls (PCBs). This experiment demonstrated that the subambient pressures required for good recovery (97 percent) of ^{14}C -PCBs resulted in substantial losses of highly volatile compounds. Ambient pressure operation of the flash evaporator resulted in acceptable recovery of ^{14}C -chloroform but poor recovery of ^{14}C -PCBs. Under both sets of conditions the carry-over of ^{36}Cl was unacceptably high.

Derivatization of Free Chlorine

Syringaldazine (Aldrich Gold Label, 99+%) was dissolved in 2-propanol at a concentration of one percent by weight. This solution was diluted as necessary to measure the spectral characteristics of the reagent and its oxidation product. Syringaldazine reacts with hypochlorous acid to form an oxidation product. The oxidation product forms a purple dye which is useful as a colorimetric measure of the concentration of "free" chlorine or hypochlorous acid in water. The colored product resulting from the oxidation of syringaldazine by chlorine absorbs in the visible region of the spectrum with an absorption maxima centered at a wavelength of 530 nm. Figure 3

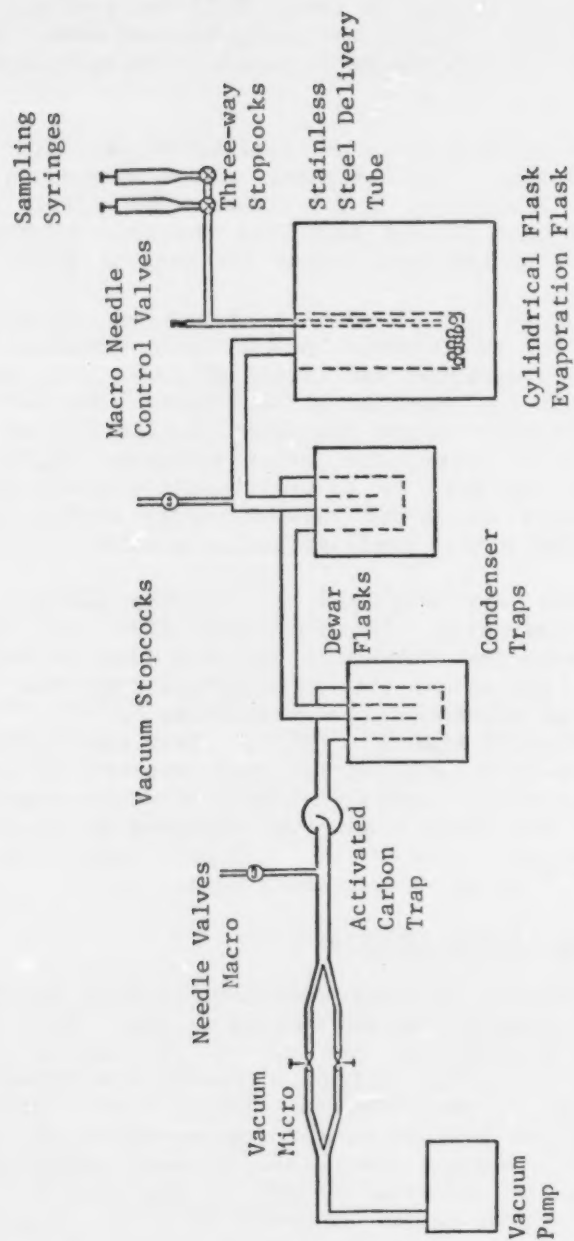


Figure 2. Model II: gravity separation flash evaporation flask.

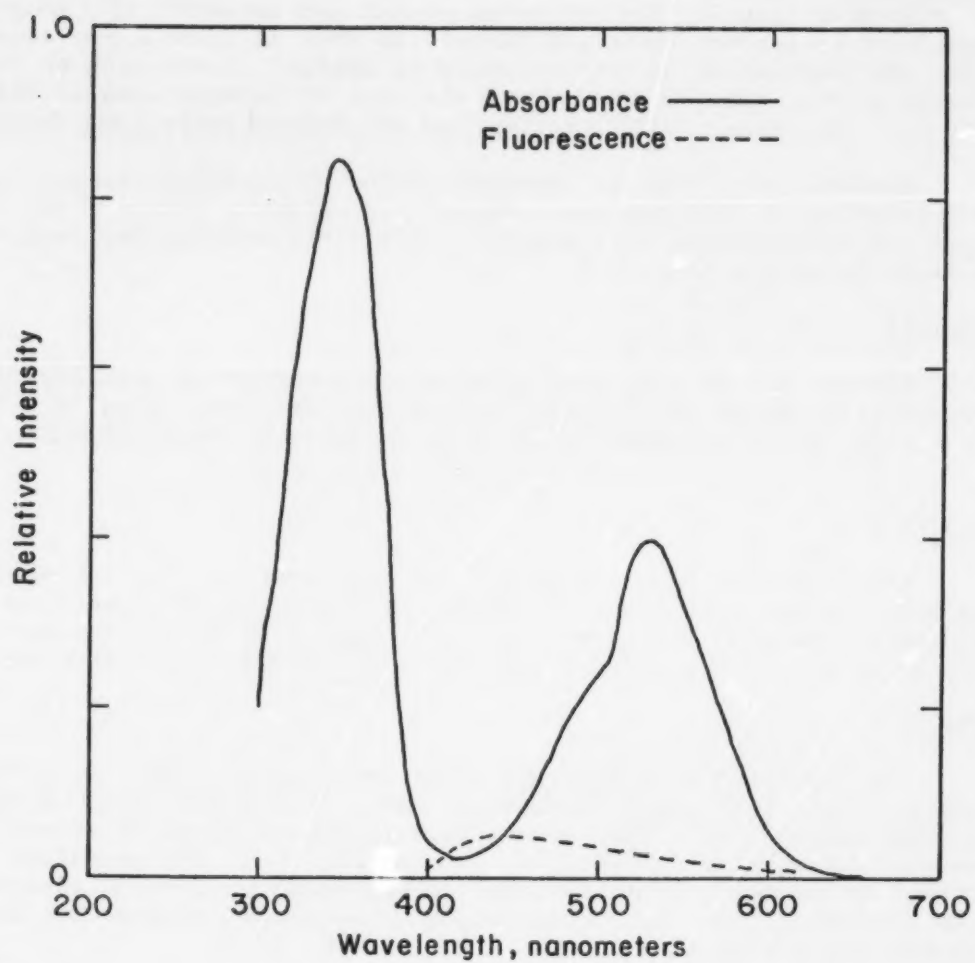


Figure 3. Absorption and fluorescence of the oxidation product of syringaldazine, pH 6.5.

illustrates the absorption and fluorescence emission spectra of the oxidation product of syringaldazine. The unoxidized reagent has a strong fluorescence at 530 nm at pH 8 or higher (Figure 4) and at a wavelength of 420 nm at pH 4 (Figure 5). The reagent fluoresces only weakly near pH 7 (Figure 6). The colored oxidation product is unstable at a pH of less than 6 or greater than 8. The oxidation product was extracted by liquid-liquid partitioning between water and benzene to free it from excess reagent so that its fluorescence properties could be studied. Extraction of the oxidation product into benzene slowed the rate of decomposition or fading of the dye. No evidence of fluorescence of the colored product was found.

Attempts were made to identify another fluorometric reagent for the determination of free chlorine. However, an extensive review of the literature and conversations with experts in the field revealed that this was not a promising avenue to pursue.

Summary

Because of the technical difficulties encountered with the System I approach, particularly with the fluorometric detection step, this line of investigation was abandoned in favor of the approach described below.

SYSTEM II

The second and more successful approach involves: (a) introduction of sample by direct injection; (b) conversion of chlorinated organics to HCl in heated quartz tube; (c) removal of water vapor from carrier gas stream; and (d) detection of HCl using a piezoelectric crystal coated with Amine 220.

Theory

The piezoelectric effect was first described in 1880. An oscillating quartz crystal, 10-16 mm in diameter and 0.15 mm thick, oscillating at an optimum frequency of 9 MHz, shows a decrease in its frequency of oscillation when a compound is adsorbed on its surface (12). The magnitude of the change in frequency is proportional to the amount of material adsorbed over its surface. There is a quantitative relationship between the frequency change, ΔF , and the mass adsorbed, ΔM_s (13,14):

$$\Delta F = 2.3 \times 10^6 \times F^2 \times \frac{\Delta M_s}{A}$$

F = frequency of crystal oscillation

M_s = mass of material adsorbed to crystal surface

A = area of crystal surface

The theoretical limit of detection of the quartz crystal is 10^{-12} g, with linear ranges of 4 to 6 orders of magnitude (generally parts per trillion up to parts per million).

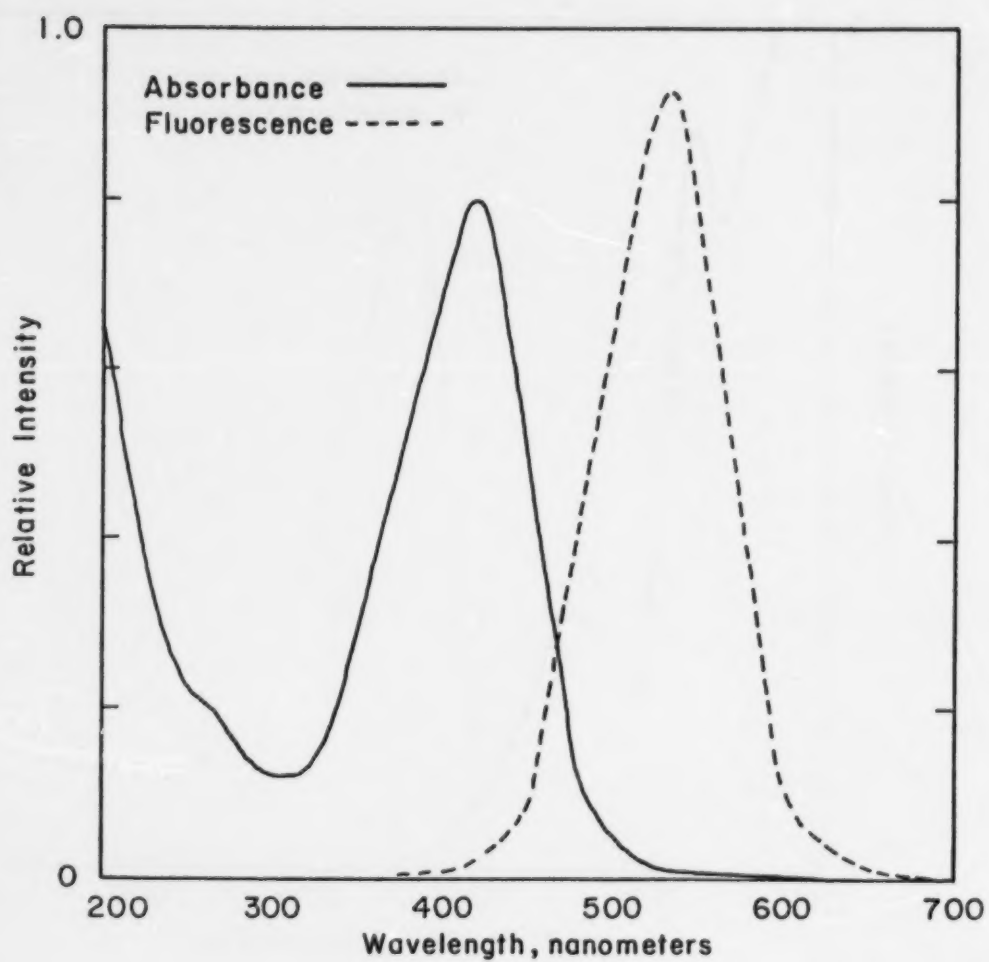


Figure 4. Absorption and fluorescence of syringaldazine, pH 10.0.

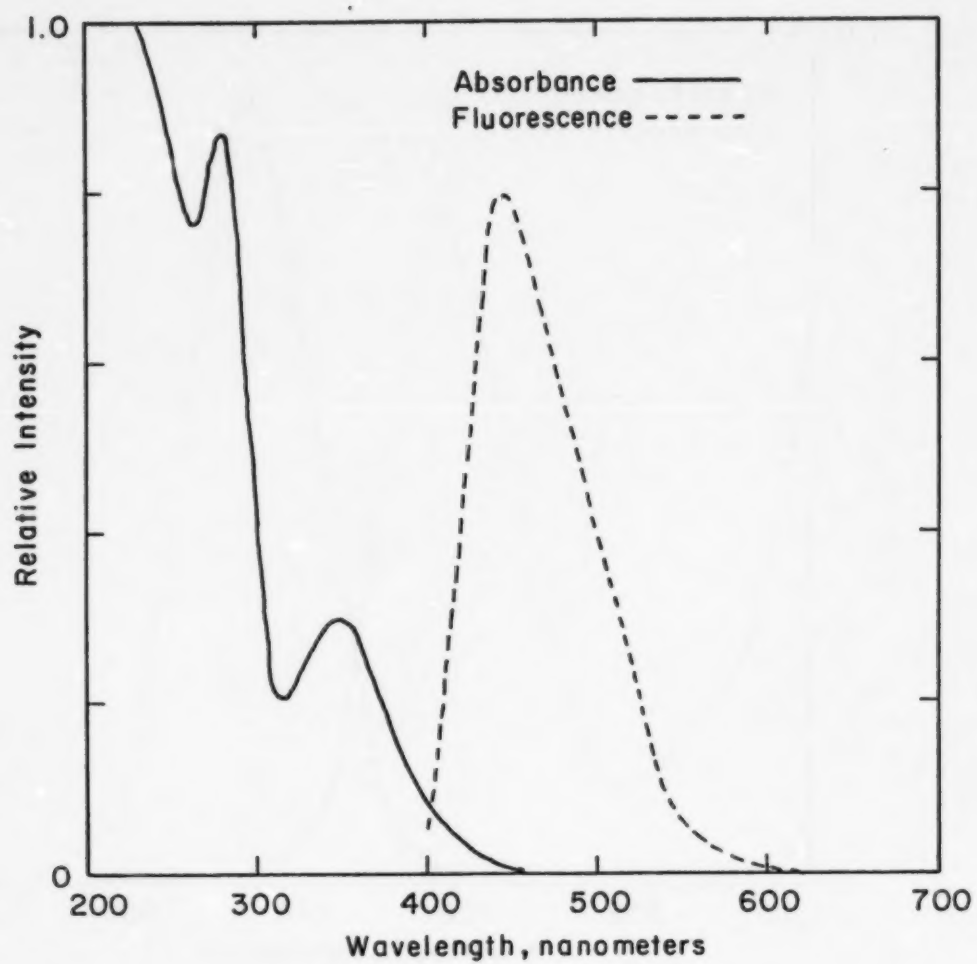


Figure 5. Absorption and fluorescence of syringaidazine, pH 4.0.

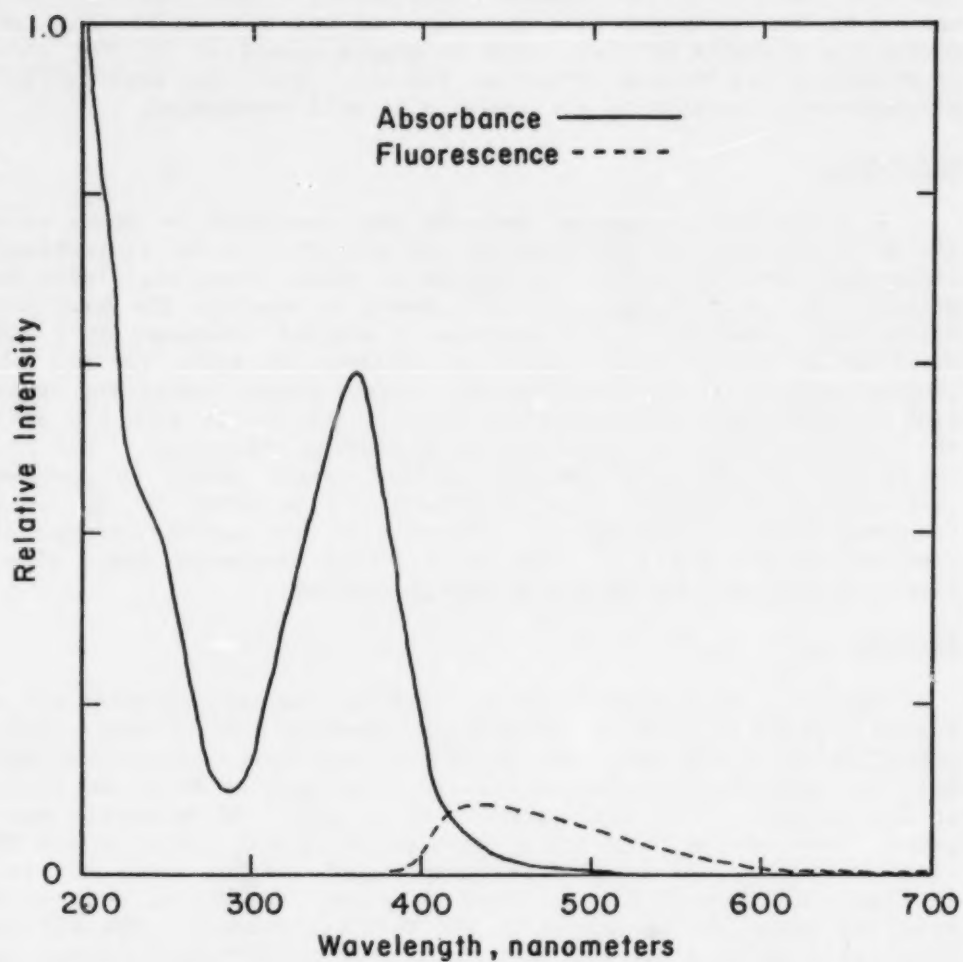


Figure 6. Absorption and fluorescence of syringaldazine, pH 7.0.

It is possible to coat crystals with materials which are selective for certain compounds. Generally, this is accomplished by dissolving the coating material in a volatile solvent and immersing the crystal surfaces in the solution for a fixed amount of time. Solvent is then driven off by gentle warming of the coated crystal. Previous detectors reported include the Moisture Analyzer^R (15) (Dupont Instruments) which has a 30 seconds response in the parts-per-million range and was used on the Martian Mariner probe; the dynamite detector which is highly selective for NO₂; and the OSHA formaldehyde and toluene detectors (16-18). Thus, the applicability of the piezoelectric crystals to air analysis is well documented.

Apparatus

A piezoelectric crystal detector was assembled as shown in Figure 7. The flow entrance of the detector was attached to the combustion/absorber train described in Figures 10 through 13 while tests were being conducted. Briefly, the power supply provides power to operate the oscillator which drives the piezoelectric crystals at a nominal frequency of 9.0 MHz. The differential piezoelectric cell is designed to split the gas stream and impinge half of it on each crystal. When a sample containing organic chlorine is combusted, the resulting chloride ion reacts with the Amine 220 on the coated crystal to form the corresponding chloramine. The increase in the weight of the material coating the crystal causes an increase in the oscillating frequency. This difference is detected by the differential frequency counter and can be presented to an analog recorder through a digital/analog convertor. The differential frequency could also be read from a digital display on the frequency counter.

Experimental

The first task undertaken in investigating this approach was to select a substrate to be used in coating the piezoelectric crystal. Criteria for selecting a coating material include a sensitive, reversible response to HCl, low response to potential interferences such as NaCl, and good adhesion to the crystal. The applicability of a number of materials was investigated. Each of the first set of test materials was coated on a 9 MHz piezoelectric crystal and exposed to known amounts of HCl using the system shown in Figure 8. The design was used to permit removal of most of the water prior to entry of the sample to the detector chamber. The HCl was introduced as 1 mL of a 500-part-per-million (volume/volume) aqueous injection. Table 1 presents the response of the crystal with each coating to this amount of HCl compared to the response to the same volume of distilled/deionized water.

Quadral, 4-aminoacetanilide, triethylenetetramine, and L-ornithene showed little or no response to HCl. The response of triphenylamine and triethanolamine were irreversible; that is, HCl was adsorbed but not released. After five replicate injections, the crystal coated with trimethylamine-HCl showed no further response. The substrate either had degraded or

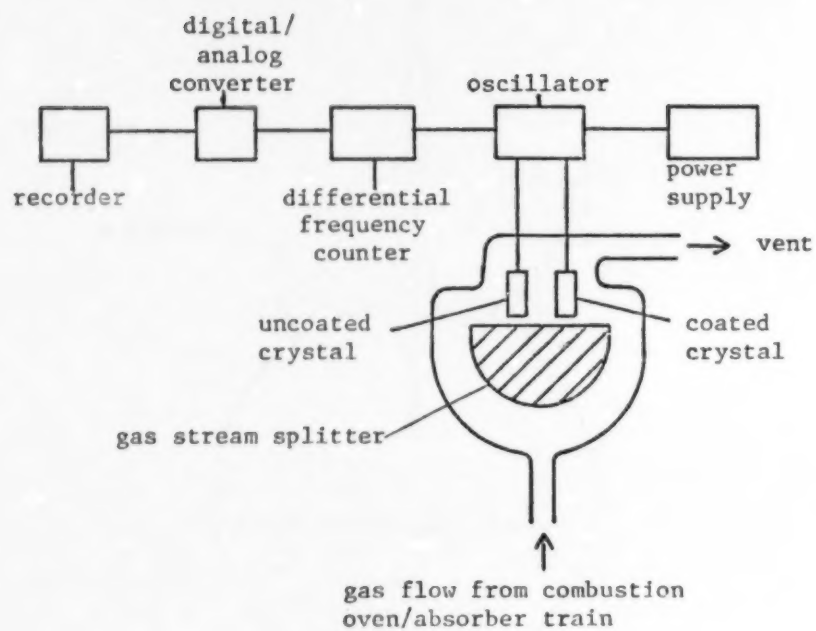


Figure 7. Schematic representation of the chlorine-specific piezoelectric detector.

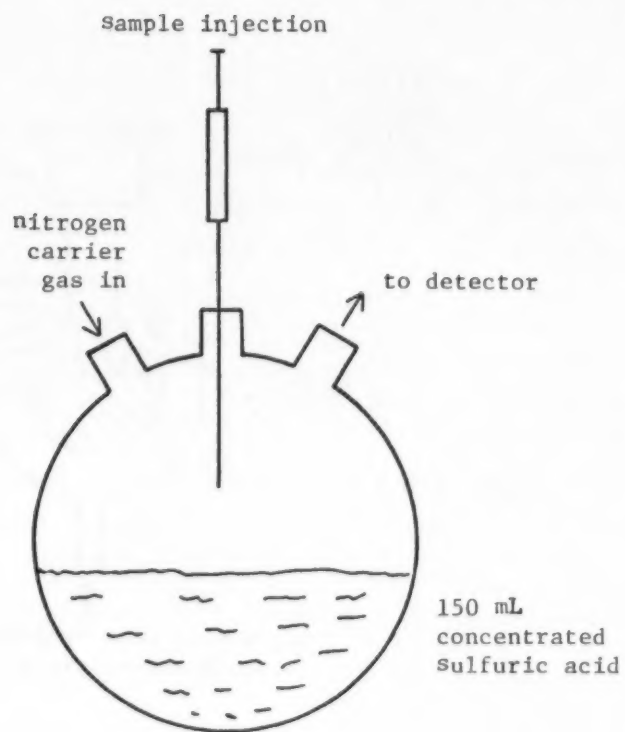


Figure 8. Schematic of procedure to test samples for suitability as coating materials for the piezoelectric crystal detector.

TABLE 1. RESULTS OF COATING SELECTION EXPERIMENTS

Coating Material	Detector Response, 1 mL H ₂ O	Δ Frequency (Hz) 1 mL H ₂ O + 500 μ g HCl
Quadrol	9	15
Triphenylamine	3	3
Triethanolamine	10	40
4-Aminoacetanilide	17	19
Triethanolamine-HCl	3	6
Tri-n-octylamine	1	280
Tri-n-hexylamine	3	110
Triethylenetetramine	3	3
L-Ornithine-HCl	18	21
Amine 220	18	960

Several other coatings were investigated which were known to be very hygroscopic. Because of this, a slightly different apparatus was used evaluate these materials to ensure more complete removal of water before the sample reached the detector. Figure 9 presents a schematic of the apparatus. A comparison of the response of the coatings to injections of laboratory air and to gaseous mixtures of dry HCl and laboratory air is shown in Table 2.

TABLE 2. RESULTS OF COATING SELECTION EXPERIMENTS WITH
HYGROSCOPIC MATERIALS

Coating Material	Detector Response, 1 mL air	Δ Frequency (Hz) 1 mL air + 3 μ g HCl
Triphenylamine	13	20
Amine 220	41	315
Trimethylamine-HCl	13	875
Triethanolamine	10	260
<u>P</u> -nitrobenzaldehyde	16	18

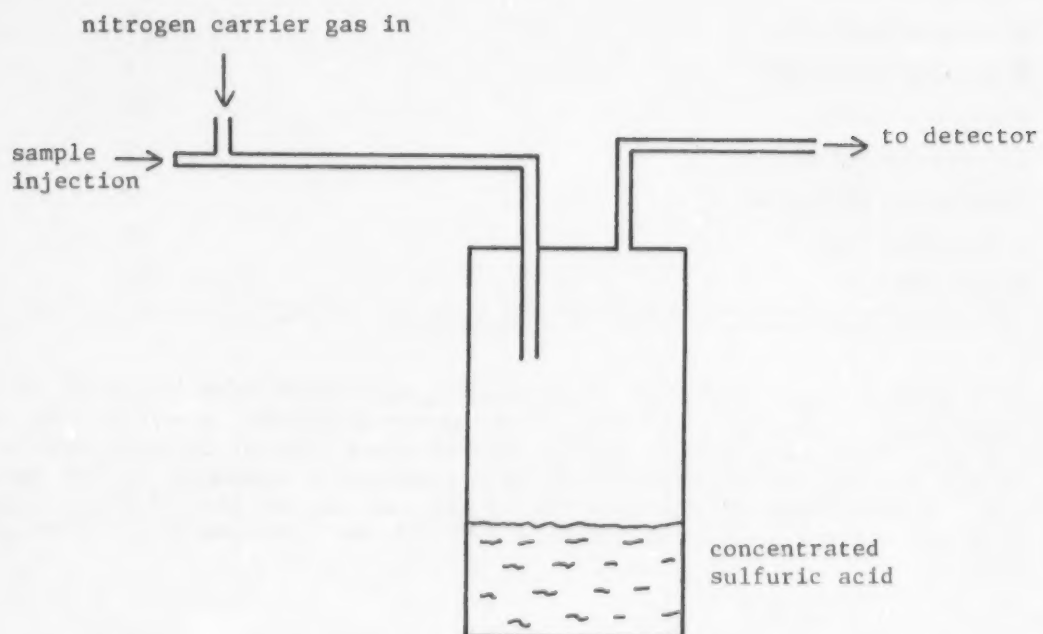
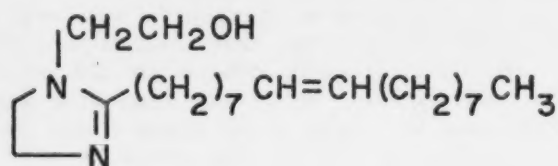


Figure 9. Schematic of apparatus used to evaluate hydroscopic coatings.

became saturated. Three coating materials, tri-n-octylamine, tri-n-hexylamine, and Amine 220 gave a good reversible response to HCl injected. Amine 220 resulted in the largest change in the crystal frequency and showed good adherence to the crystal. This substrate was selected for further testing.

The 9 MHz crystal coated with Amine 220 was exposed to several levels of SO₂ to determine if these materials cause interferences in the detection of HCl. The results of this experiment are presented in Table 3. Repeated injections of aqueous solutions of HCl containing as much as 500 parts per million NaCl (weight/volume) showed no effect from the presence of the inorganic salt.

Because of the sensitivity and specificity of the crystal with the Amine 220 coating, it was chosen for use in this system and used in all other studies. Amine 220 is a commercial product available through Pfaltz and Bauer, Stamford, Connecticut. Its chemical name is 2-(8-heptadecenyl)-2-imidazoline-1-ethanol, with a molecular formula of C₂₂H₄₂N₂O and a molecular weight of 350.57. Its structure is given below:



The next task was to interface the detector to the furnace in which HCl (or HBr or HI) was to be generated from halogenated organics in the aqueous sample. Initial investigations involved injection of aqueous solutions into a heated quartz tube coupled to the detector cell by simple ground glass fittings. Using this configuration, injections of laboratory air produced large responses. It was determined that this was due to "thermal shock"; that is, rapid expansion of the aqueous injection in the heated quartz tube. Moving the detector cell farther away to minimize this effect resulted in condensation of water on the crystal. Heating the crystal to prevent condensation caused the Amine 220 to bleed from the crystal which changed the response characteristics and caused a serious drift in the baseline. It was necessary, therefore, to introduce a component in the system between the oven and the detector which would remove water from the carrier gas stream.

TABLE 3. RESULTS OF EXPOSURE OF AMINE 220 COATED CRYSTAL TO SO₂

Amount SO ₂ Injected ppm (v/v)		Detector Response* 5 mL	ΔFrequency (Hz) 5 mL + SO ₂
100	(1.3 μg)	360	368
1.0	(0.013 μg)	360	364
0.1	(0.0013 μg)	360	363

* This represents an injection of 5 mL of laboratory air. No attempt was made to remove chlorinated compounds from the sample. Response is presumed to be due to background levels of HCl in the laboratory.

The first approach investigated was the use of a trap containing a desiccating material between the oven and the detector. Absorbance of water by calcium carbide resulted in the formation of acetylene, which seemed to strip the coating from the crystal; therefore, this approach was abandoned. The applicability of phosphorous pentoxide was evaluated next. Although water was effectively removed by this technique, HCl was also trapped. Heating the trap to 95°C did not result in the release of HCl, and this technique was also abandoned. Anhydrous magnesium perchlorate was investigated next. Water and HCl were both trapped and HCl was released slowly when the trap was heated to 195°C. The response of the detector using this material was not reproducible. Water and HCl were both irreversibly absorbed by a calcium sulfate trap.

Since trapping water on a solid material was not successful, the applicability of a concentrated sulfuric acid scrubber was investigated. The first scrubber configuration which was evaluated is illustrated in Figure 10. The breakthrough capacity of the scrubber was evaluated by placing a tube containing calcium sulfate downstream of the scrubber and repeatedly injecting 0.1 mL of distilled deionized water into the system. The glass beads were coated with fresh H₂SO₄ after each injection. After 20 injections, totaling 2 g of water, the calcium sulfate tube showed no weight gain. This demonstrates that the efficiency of the scrubber for water was greater than 99.9 percent. Injections of aqueous solutions of HCl yielded a minimal response. When the output of the detector was displayed on a chart recorder, a low broad peak was observed. This suggests that the HCl was being absorbed by the scrubber and gradually bled off by the action of the carrier gas.

On the assumption that this problem was caused by the large dead volume of the scrubber, another configuration was designed and tested. This scrubber is pictured in Figure 11. A significant detector response was

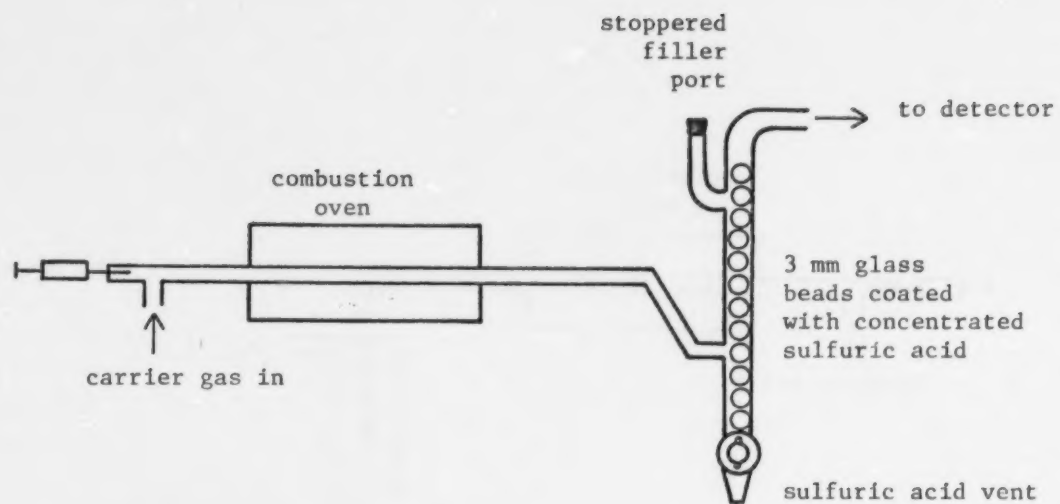


Figure 10. Configuration of the first concentrated sulfuric acid scrubber evaluated.

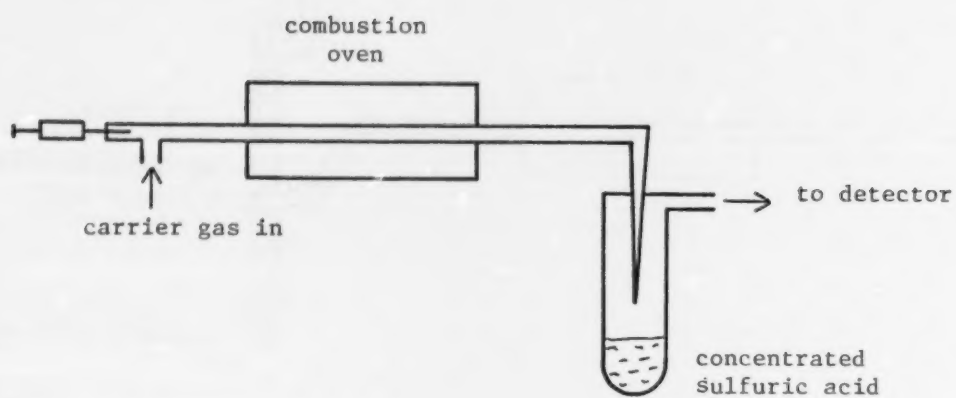


Figure 11. Configuration of the second concentrated sulfuric acid scrubber evaluated.

observed with the injection of 0.1 mL of distilled deionized water indicating that the capacity of the scrubber had been exceeded. Use of a larger volume scrubber, as shown in Figure 12, produced the same results. Therefore, a modification of the configuration shown in Figure 10 must be evaluated for incorporation into the instrument.

Finally, the efficiency of the conversion of chlorinated organics to HCl was investigated. Using an oven temperature of 600°C and an oxygen flow rate of 60 mL/min, aqueous solutions of HCl and of CHCl_3 were injected into the system. Chloroform solutions were prepared at one-third the concentration of HCl solutions so that injections of equal volumes should produce the same response. Over the three orders of magnitude that the system was evaluated, the response to chloroform was consistently 10 percent of that expected based on analysis of HCl. To improve the sensitivity of the instrument, the efficiency of the conversion step must be improved.

Results

Funding constraints made it impossible to evaluate additional parameters. The specific components of the system which require further investigation are discussed in Section 3 of this report.

At the time work was terminated, the coated piezoelectric crystal detector had been demonstrated to be sensitive enough to fulfill the original grant objectives. Coated with Amine 220, the crystal is capable of detecting approximately 100 pg of HCl. The detector was also demonstrated as being insensitive to as much as 500 parts per million (weight/volume) of inorganic salt and as much as 1.3 $\mu\text{g SO}_2$. The crystals are very inexpensive (approximately \$20.00, coated or uncoated).

With this detector system, sample preconcentration is not required and the analysis from start to finish is only about five minutes. Additional development of this system may provide USEPA with a significant improvement in TOX methodology and an instrument which provides rapid, reliable data on the levels of chlorinated organics in aqueous samples. Per sample analysis costs could be reduced to approximately \$25.00.

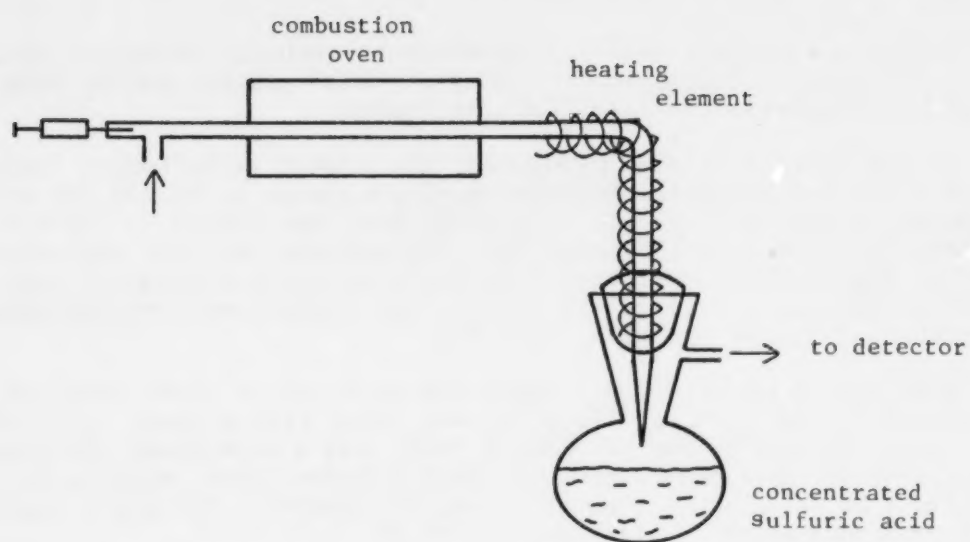


Figure 12. Concentrated sulfuric acid scrubber with larger volume.

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